Effects of Interfacial Charge Transfer on the Effective Surface Recombination Velocity of Si/Liquid Contacts

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Photoconductivity decay data have been obtained for NH4F(aq)-etched Si(111) and for air-oxidized Si(111) surfaces in contact with solutions of CH3OH or tetrahydrofuran (THF) that contained either ferrocene+/0 (Fc+/0), bis(pentamethylcyclopentadienyl)Fe+/0 (Me10Fc+/0), I2, or cobaltocene+/0 (CoCp2+/0). Carrier decay measurements were made under both low-level and high-level injection conditions using a contactless rf photoconductivity decay apparatus. When in contact with electrolyte solutions having either relatively positive (¿ 0 V vs SCE) or very negative (CoCp2+/0) Nernstian redox potentials, Si surfaces exhibited low effective surface recombination velocities . In contrast, surfaces that were exposed only to N2(g) ambients or to electrolyte solutions that contained mild oxidants (such as Me10Fc+/0) showed differing rf photoconductivity decay behavior depending on their different surface chemistry. Specifically, surfaces that possessed Si-OCH3 bonds produced by reaction of H-terminated Si with CH3OH-Fc+/0 showed lower surface recombination velocities in contact with N2(g) or in contact with CH3OH-Me10Fc+/0 solutions than did NH4F(aq)-etched, H-terminated Si(111) surfaces in contact with these same ambients. Similarly, the CH3OH-Fc+/0-treated surfaces showed lower surface recombination velocities than H-terminated Si surfaces that had been exposed to CH3OH-I2 or THF-I2 solutions. These results can all be consistently explained through reference to the electrochemistry of Si/liquid contacts. In conjunction with prior measurements of the near-surface channel conductance for p+-n-p+ Si structures in contact with CH3OH-Fc+/0 solutions, the data reveal that formation of an inversion layer (i.e., an accumulation of positively charged mobile carriers at the surface) on n-type Si, and not a reduced density of surface electrical trap sites, is primarily responsible for the long charge-carrier lifetimes observed for Si surfaces in contact with CH3OH or THF electrolytes containing I2 or Fc+/0. Similarly, formation of an accumulation layer (i.e. an accumulation of negatively charged mobile carriers at the surface) consistently explains the low effective surface recombination velocity of the Si/CH3OH-CoCp2 contact. Furthermore, anodically activated alkoxylation in the presence of the one-electron oxidant Fc+ in alcohol solvents produces surfaces with lower surface recombination velocities than does exposure to CH3OH-I2 or THF-I2 solutions. These conclusions have been supported by detailed digital simulations of the photoconductivity decay dynamics for semiconductors that are in inversion or accumulation conditions while in contact with redox-active electrolytes. The data also suggest that an analogous charge-transfer related effect plays a significant role in producing the low effective surface recombination velocities that are observed for NH4F(aq)-etched, H-terminated Si(111) surfaces in contact with highly acidic aqueous solutions.